Canadian Water Quality Guidelines for the Protection of Aquatic Life

BORON

Boron (CAS Registry Number 7440-42-8) is ubiquitous in the environment, occurring naturally in over 80 minerals and constituting 0.001% of the Earth's crust (U.S. EPA, 1987). The chemical symbol for Boron is B with an atomic weight of 10.81 g mol^{-1} (Budavari et al., 1989; Weast, 1985; Lide, 2000; Clayton and Clayton, 1982; Sax, 1984; Windholz, 1983; Moss and Nagpal, 2003). Boron is not found as a free element in nature.

Sources to the environment: The highest concentrations of boron are found in sediments and sedimentary rock, particularly in clay rich marine sediments. The high boron concentration in seawater (4.5 mg B L^{-1}), ensures that marine clays are rich in boron relative to other rock types (Butterwick et al., 1989). The most significant source of boron is seasalt aerosols, where annual input of boron to the atmosphere is estimated to be 1.44 Tg B $year^{-1}$, where Tg = 10^{12} g (Park and Schlesinger, 2002). In addition to atmospheric deposition, boron is also released into the environment very slowly at low concentrations by natural weathering processes. Due to the extensive occurrence of clay-rich sedimentary rocks on the Earth's land surfaces, the majority of boron mobilized into soils and the aquatic environment by weathering probably stems from this source. Natural weathering is estimated to release more boron into the environment than industrial sources (Butterwick et al., 1989) as boron is tied up in many industrial products such as glass. Natural weathering (chemical and mechanical) of minerals from carbonate rocks has been estimated to mobilize 0.193 Tg B $year^{-1}$ (Park and Schlesinger, 2002). Other natural sources include volcanic emissions (0.017-0.022 Tg B yr^{-1}), soil dust (0.017-0.033 Tg B yr^{-1}), and plant aerosols (0.004 Tg B yr^{-1}). Volcanic emissions release boric acid and boron trifluoride; therefore, the concentrations of boron in water in volcanic regions are high (Health Canada, 1990). The evaporation of sea water from closed basins is a commercial source of boron (Durocher, 1969). The estimated amounts of boron introduced into the atmosphere as a result of fossil fuel combustion, biomass burning and other human activities (e.g. manucturing and incineration) are 0.20, 0.26-0.43, and 0.07 Tg B/yr, respectively (Park and Schlesinger, 2002). The wet deposition of boron over the continents is estimated to be approximately 0.50 Tg B/yr, where rainwater from continental sites contains less boron when compared to boron from coastal and marine sites (Park and Schlesinger, 2002).Natural weathering (chemical and mechanical) of boron-containing rocks is a major source of boron compounds in water (Butterwick et al., 1989) and on land (Park and Schlesinger, 2002). The amount of boron released into the aquatic environment varies greatly depending on the surrounding geology. Boron compounds also are released to water in municipal sewage and in waste waters from coal-burning power plants, irrigation, copper smelters and industries using boron (ATSDR, 1992; Howe, 1998). With respect to Canadian wastewater discharges, a literature review was conducted to characterize the state of knowledge of municipal effluent (Hydromantis Inc., 2005). The study reported that boron releases from two Western Canadian wastewater treatment plants, releasing either raw or primary treated effluent, ranged from 110 to 180 µg L^{-1}. Therefore, the study indicates that municipal wastewater effluent in Canada is less likely to be a source, and boron concentrations in water are more likely dependant on the leaching of boron from the surrounding geology (WHO, 2003).

Boron is produced anthropogenically by the chemical reduction of boron compounds with reactive metals, either by non-aqueous electrolytic reduction or thermal decomposition. Highly purified boron is produced by zone-refining or other thermal techniques (Stokinger, 1981; U.S. Bureau of Mines, 1989). Borax, found in playa (intermittent) lakes and other evaporite deposits, is used to produce refined sodium borate compounds and boric acid (ATSDR, 1992).

Table 1. Canadian Water Quality Guidelines (CWQG) for Boron for the Protection of Aquatic Life (mg L^{-1})

	Long-Term Exposure	Short-Term Exposure
Freshwater	1.5	29
Marine	NRG	NRG

NRG = no recommended guideline

Uses: Borates and boric acids are used in glass manufacturing (fibreglass, borosilicate glass, enamel, frit, and glaze), soaps and detergents, flame retardants, and neutron absorbers for nuclear installations (WHO, 2003). Boric acid, borates and perborates have been used in mild antiseptics, cosmetics, pharmaceuticals, as antioxidants for soldering, cleaning products/ detergents, boron neutron capture therapy and agricultural fertilizers (WHO, 2003). Boron compounds are also used in the leather, textile, paint and wood-processing industries (Health Canada, 1990). Borax (or sodium tetraborate, $Na_2B_4O_7$, molecular weight of 381.37 g mol^{-1}) and boric acid (BH_3O_3, molecular weight of 61.833 g mol^{-1}) are used as insecticides in Canada (Health Canada, 1990). Borax is also used extensively as a cleaning agent and an antimicrobial agent (Health Canada, 1990).

Ambient concentrations: The majority of the Earth's boron is found in the oceans, with an average concentration of 4.5 mg L^{-1} (Weast, 1985). The amount of boron in fresh water depends on factors such as the proximity to marine coastal regions, inputs from industrial and municipal effluents and the geochemical nature of the drainage area (Butterwick et al., 1989). Naturally-occurring boron is present in groundwater, primarily as a result of leaching from rocks and soils containing borates and borosilicates (WHO, 2003). High boron concentrations are indicative of boron-rich deposits. Typical boron concentrations are less than 0.1 mg L^{-1}, with a 90th percentile concentration of 0.4 mg L^{-1} (WHO, 1998). The National Water Quality Monitoring Office of Environment Canada provided boron concentration data measured in surface waters from various locations across Canada (C. Lochner 2008, pers. com.). Boron concentrations ranged from 0.0001-0.951 mg L^{-1} (extractable) in Nova Scotia, 0.008-0.13 mg L^{-1} (extractable) and 0-0.607 mg L^{-1} (total) in Newfoundland, and 0.0001-0.402 mg L^{-1} (extractable) in New Brunswick. For Ontario, data was provided for the Great Lakes and Great Lake connecting channels. Total boron concentrations ranged from 0.006-0.011 mg L^{-1} in Lake Superior, 0.004-0.018 mg L^{-1} in Lake Huron, 0.007-0.011 mg L^{-1} in Georgian Bay, 0.015-0.031 mg L^{-1} in Lake Erie and 0.018-0.077 mg L^{-1} in Lake Ontario. Total boron concentrations measured in the St. Clair River, Niagara River and St. Lawrence River were 0.009-0.021 mg L^{-1}, 0.018-0.032 mg L^{-1}, and 0.02-0.032 mg L^{-1}, respectively. Surface water total boron concentrations ranged from 0.0052-0.271 mg L^{-1} in Manitoba, 0.0001-2.58 mg L^{-1} in Saskatchewan, 0.0001-0.082 mg L^{-1} in Alberta, 0.0001-2.3 mg L^{-1} in the Northwest Territories, and 0.0001-0.006 mg L^{-1} in the Yukon. In Quebec, recent data (2004-2006) were obtained in clean conditions, on the acid soluble fraction. Of the 23 rivers sampled, the median boron concentrations ranged from 0.0021 to 0.058 mg L^{-1} with a median concentration for all the rivers of 0.0063 mg L^{-1} (MDDEP, 2007 unpublished data).

Properties, Speciation and Fate: Elemental boron is insoluble and inert in aqueous solutions (Weast, 1985; Windholz, 1983; Clayton and Clayton, 1982; Hawley, 1981; Budavari et al., 1989; U.S. EPA, 1975). Boron compounds rapidly transform to borates, the naturally occurring forms of boron, when exposed to water. However, no further degradation is possible. The only significant mechanism expected to influence the fate of boron in water is adsorption-desorption reactions with soil and sediment (Rai et al., 1986). The extent of boron adsorption depends on the pH of the water and concentration of boron in solution. The greatest adsorption is observed between a pH of 7.5 and 9.0 (WHO, 2003). In natural waters, boron forms stable species and exists primarily as undissociated boric acid [$B(OH)_3$] and complex polyanions (*e.g.*, $B(OH)_4^-$) (Health Canada, 1990; Howe, 1998; WHO, 2003). These forms of boron are highly soluble and not easily removed from solution by natural mechanisms. Borate and boric acid are in equilibrium depending on the pH of the water. At an acidic pH, boron exists in solution mainly as undissociated boric acid, whereas at alkaline pH it is present as borate ions (Howe, 1998).

Bioaccumulation: Boron has been shown to accumulate in aquatic plants (Schuler, 1987; Saiki et al., 1993), which may be evidence for its importance in plant nutrition. Fernandez et al. (1984) examined the bioaccumulation of boron in green alga (*Chlorella pyrenoidosa*). After seven days, the bioconcentration factor (BCF) for three concentration levels ranged from four to five. In a study conducted by Davis et al. (2002), duckweed (*Spirodella polyrrhiza*) did not accumulate significant amounts of boron from the treatment solutions. However, Glandon and McNabb (1978) found that duckweed (*Lemna minor*) did bioaccumulate boron compared to other hydrophytes (*e.g., Ceratophyllum demersum*). A curvilinear relationship was observed between ambient boron concentrations and concentrations in the plant tissues, suggesting that both active and passive transport of boron across plant root membranes occurs in this species. Frick (1985) found that pH affected the bioaccumulation of boron by duckweed (*Lemna minor*). Despite a tendency to accumulate in plants and algae, boron does not appear to biomagnify through the food chain (Wren et al., 1983; Saiki et al., 1993). The BCFs for boron in freshwater plants, fish and invertebrates were estimated to be less than 100 (Thompson et al., 1972). Experimental BCFs for fish have ranged between 52 and 198 (Tsui and McCart, 1981). A study conducted by Suloway et al. (1983) examined the bioaccumulation potential of the components of coal fly ash extract in fathead minnows (*Pimephales promelas*) and green sunfish (*Lepomis cyanellus*). The BCF for boron was 0.3 for both species. These BCF values suggest that boron does not significantly bioconcentrate or biomagnify in the aquatic environment.

Method Detection Limits: Various analytical methods are available to accurately detect boron levels in water ranging from 0.01 mg $L^{-1}$to 10 mg L^{-1} (Health Canada, 1990). Inductively coupled plasma-mass spectrometry (ICP-MS) is typically used to determine the concentration of boron in aquatic samples. Environment Canada's National Laboratory for Environmental Testing (NLET) analyzes for trace metals, such as boron, in water using ICP-MS with a method detection limit of 0.0005 mg L^{-1} (J. Carrier 2008, pers. com.). The Ontario Ministry of the Environment, Canadian Association for Environmental Analytical Laboratories (CAEAL) accredited method (E3474) determines the concentration of trace metals in surface and groundwater by dynamic reaction cell (DRC) using inductively coupled plasma-mass spectrometry (ICP-MS) (R. Moody 2008, pers. com.). The current MOE laboratory detection limit in water is 0.0002 mg L^{-1}.

Essentiality and Deficiency: Boron is an essential nutrient for the growth of higher plants, and has therefore been used as an additive to B-deficient soils (Eisler, 1990). The potential essential effects of boron have been studied on a variety of freshwater fish, amphibians, invertebrates and plants. At lower concentrations, boron has been found to be beneficial to some freshwater organisms. For instance, the addition of 0.4 mg L^{-1} of boron to ponds used for raising carp increased production by 7.6% (Avetisyan, 1983). Furthermore, Fort et al. (1999) found that boron was nutritionally essential for reproduction and development in frogs (*Xenopus laevis*). Rowe et al. (1998) found that the shape of the dose-response curve in rainbow trout (*Oncorhynchus mykiss*) and zebrafish follows the U-shaped adverse response of an essential nutrient. This shape reflects effects of exposure to boron concentrations below the level to meet physiological requirements and toxic effects due to exposure to high concentrations of boron that exceed the threshold for safety. For rainbow trout embryos, long-term exposures below 0.097 mg L^{-1} impaired embryonic growth. In addition, zebrafish (*Danio rerio*) exposed to boron concentrations below 0.0022 mg L^{-1} experienced zygote death (Rowe et al., 1998). In order to prevent adverse health effects to organisms caused by a deficiency of essential chemicals, recommended threshold levels for boron should not fall below the level required by the organism to remain healthy.

Toxicity-modifying factors: The toxicity of metals to aquatic organisms is often modified by water hardness. Some research has indicated that there does not appear to be any significant interaction between water hardness and boron toxicity (Birge and Black, 1977; Laws, 1981; Hamilton and Buhl, 1990; Maier and Knight, 1991). Studies conducted by the British Columbia Ministry of the Environment Land and Parks (MELP, 1996) found that an increase in water hardness decreased the toxicity of boron to both the amphipod (*Hyalella azteca*) and the water flea (*Daphnia magna*), but not so for coho salmon (*Oncorhynchus kisutch*), rainbow trout (*Oncorhynchus mykiss*) and the freshwater midge (Chironomus tentans). Laws (1981) found that there was no interaction between sulphate and boron in natural aquatic ecosystems. It is hypothesized that boron attenuation may occur via complexation with organic compounds or adsorption to particulate matter. Several studies have shown that the low-level effects observed in reconstituted laboratory water are not predictive of the much higher effect levels found under natural water exposure conditions (Butterwick et al., 1989; Black et al., 1993). However, the specific component of the water chemistry responsible for toxicity modification is unknown.

Toxicity: Short-term severe effect toxicity concentrations (24-96h LC_{50}s) in fresh waters ranged from 4.6 mg L^{-1} for the bluegill sunfish (*Lepomis macrochirus*) (Turnbull et al., 1954) to >1,000 mg L^{-1} for both the coho salmon (*Oncorhynchus kisutch*) (Hamilton and Buhl, 1990) and the Chinook salmon (*Oncorhynchus tshawytscha*) (Hamilton and Buhl, 1990). In the case of invertebrates, severe effect toxicity concentrations (48-96h LC_{50}s) ranged from 21.3 mg L^{-1} for the water flea (*Daphnia magna*) (MELP, 1996) to 1,376 mg L^{-1} for the midge (*Chironomus decorus*) (Maier and Knight, 1991).

Hamilton and Buhl (1990) conducted 24 and 96h boron exposures using different life stages of the Chinook salmon (*Oncorhynchus tshawytscha*) and found that boron was relatively non-toxic (24h LC_{50} >1,000 mg L^{-1}, 96h LC50 566 to >1,000 mg L^{-1}) to both life stages (swim-up fry and advanced fry). Hamilton (1995) also tested the effects of exposing three life stages (swim-up fry and two sizes of juveniles) of the Colorado squawfish (*Ptychocheilus lucius*), razorback sucker (*Xyrauchen texanus*) and bonytail (*Gila elegans*) to boron. Even though boron was reported as being practically non-toxic (96h LC_{50}s >100 mg L^{-1}), the swim-up stage was more sensitive than the two older life stages tested (Hamilton, 1995).

Long-term exposure is defined as being ≥7d for fish and invertebrates and ≥24h for aquatic plants and algae. In fresh water, long term no-effect concentrations (NOECs) ranged from 0.001 to 26.5 mg L^{-1} for fish, 7.04 to 100 mg L^{-1} for amphibians, 4.67 to 27 mg L^{-1} for invertebrates, and 0.4 to 50 mg L^{-1} for plants. Long term low-effect concentrations (LOECs) ranged from 9.6 to 96 mg L^{-1} for amphibians, 9.3 to 100 mg L^{-1} for invertebrates, and 3.5 to 171 mg L^{-1} for plants. In the case of fish, the lowest reported value was a rainbow trout (*Oncorhynchus mykiss*) 28d LOEC of 0.01 mg L^{-1} (Birge and Black, 1977) whereas the highest reported value was a 60d LOEC of 88 mg L^{-1} for the fathead minnow (*Pimephales promelas*) (Butterwick et al., 1989). Compared with other research, various Birge and Black studies (Birge and Black , 1977; 1981) have consistently found very low boron concentration toxicity levels for a variety of aquatic species. Other scientists and studies have not been able to reproduce these values using similar conditions and species (Moss and Nagpal, 2003). These data points are considered outliers and were not considered in the development of the British Columbia Ministry of Water, Land and Air Protection guideline for boron for the protection of aquatic life (1.2 mg L^{-1}) and were not considered for CWQGPAL development. Discluding these Birge and Black studies (1977, 1981), the lowest reported LOEC for a fish species was the 28d LOEC (mortality at hatching) of 1.34 mg L^{-1} for the rainbow trout (Black et al., 1993). Black et al. (1993) also reported 36d LOECs (mortality at 8d post-hatch and teratogenesis at 8d post-hatch) of 1.34 mg L^{-1} for the rainbow trout.

In the case of long-term exposures with amphibians, the leopard frog (*Rana pipiens)* displayed greatest sensitivity, with a 7.5d LC_{01} of 3 mg L^{-1} (Birge and Black 1977). For long-term exposures with invertebrates, the water flea *Daphnia magna* shows greatest boron sensitivity with an immobilization threshold concentration of <0.38 mg L^{-1} (McKee and Wolf, 1963). The most sensitive aquatic plant was the blue green algae (*Anacystis nidulans*) with a NOEC (growth) ranging from 0.01 to 4.0 mg L^{-1} (Martinez et al 1986 In Eisler 1990).

Water Quality Guideline Derivation: The short-term and long-term freshwater Canadian water quality guidelines (CWQGs) for short-term and long-term exposure for boron for the protection of aquatic life were developed based on the CCME protocol (CCME 2007). Both the short-term and long-term guidelines were developed using the statistical (Type A) approach. Marine toxicity data was not evaluated.

Short-term Freshwater Quality Guideline: Short-term exposure guidelines provide information on the impacts of severe but transient events and are derived using severe effects data (such as lethality) of defined short-term exposure periods (24-96h). These guidelines identify estimators of severe effects to the aquatic ecosystem and are intended to give guidance on the impacts of severe, but transient, situations (e.g., spill events to aquatic receiving environments and infrequent releases of short-lived/nonpersistent substances). Short-term exposure guidelines *do not* provide guidance on protective levels of a substance in the aquatic environment, as short-term exposure guidelines are levels which *do not* protect against adverse effects, but rather indicate the level where severe effects are likely to be observed.

The minimum data requirements for the Type A guideline approach were met, and a total of 13 data points (all LC_{50} values) were used in the derivation of the guideline (Table 2). These 13 data points were retrieved from toxicity studies meeting the requirements for primary and secondary data, according to CCME (2007) protocol. Each data point was ranked according to sensitivity, and its centralized distribution on the species sensitivity distribution (SSD) was determined using the Hazen plotting position (estimate of the cumulative probability of a data point). Intra-species variability was accounted for by taking the geometric mean of the studies considered to represent the most sensitive lifestage and endpoint.

Of the six models tested, the log-Gompertz model fit the data best (Figure 1). The equation of the fitted log-Gompertz model is of the form:

$$y = 1 - e^{-e\left(\frac{x - 2.5319}{0.3609}\right)}$$

Where x is the log (concentration) and y is the proportion of species affected.

Summary statistics for the short-term SSD are presented in Table 3. The 5th percentile on the short-term SSD is 29 mg L^{-1} with approximate 95% confidence limits on this mean of 15 and 55 mg L^{-1}. The CWQG is defined as the 5th percentile on the SSD.

Therefore, the short-term exposure benchmark concentration indicating the potential for severe effects (e.g. lethality or immobilization) to sensitive freshwater/marine life during transient events is 29 mg L^{-1}, for boron.

Table 2. Endpoints used to determine the short-term CWQG for boron.

Species	Endpoint	Concentration (mg B·L^{-1})
Fish		
Lepomis macrochirus	24h LC_{50}	4.6
Pimephales promelas	96h LC_{50}	64.3
Xyrauchen texanus	96h LC_{50}	233
Ptychocheilus lucius	96h LC_{50}	279
Gila elegans	96h LC_{50}	280
Oncorhynchus mykiss	96h LC_{50}	351.7*
Oncorhynchus kisutch	96h LC_{50}	372.9*
Oncorhynchus tshawytscha	96h LC_{50}	566
Gambusia afinis	96h LC_{50}	632*
Invertebrates		
Daphnia magna	48h LC_{50}	101.2*
Chironomus tentans	96h LC_{50}	136.7*
Hyalella azteca	96h LC_{50}	141.1*
Chironomus decorus	48h LC_{50}	1,376

*Value shown is the geometric mean of comparable values

Long-term Freshwater Quality Guideline: Long-term exposure guidelines identify benchmarks in the aquatic ecosystem that are intended to protect all forms of aquatic life for indefinite exposure periods (≥7d exposures for fish and invertebrates, ≥24h exposures for aquatic plants and algae).

Table 3. CWQG short-term exposure for Boron resulting from the SSD method.

	Concentration
SSD 5th percentile	29 mg L^{-1}
Lower 95% confidence limit	15 mg L^{-1}
Upper 95% confidence limit	55 mg L^{-1}

The minimum data requirements for the Type A guideline approach were met, and a total of 28 data points (NOEC, EC_{10}, MATC and LOEC data) were used in the derivation of the guideline (Table 4). Toxicity studies meeting the requirements for primary and secondary data, according to CCME (2007) protocol, were ranked according to sensitivity. Centralized positions on the species sensitivity distributions (SSD) were determined using the Hazen plotting position. Intra-species variability was accounted for by taking the geometric mean of the studies considered to represent the most sensitive lifestage and endpoint.

Of the six models tested, the log-Normal distribution function (with a mean [μ] of 1.1443 and a standard deviation [σ] of 0.5984) fit the data best (Figure 2). The equation of the fitted log-Normal distribution function is

$$y = \Phi\left(\frac{x - 1.1443}{0.5984}\right)$$

Where x is the log (concentration) and y is the proportion of species affected. Φ is the symbol representing normal distribution.

Table 4. Endpoints used to determine the long-term CWQG for boron.

Species	Endpoint	Concentration (mg B·L^{-1})
Fish		
Oncorhynchus mykiss	87d NOEC (embryo survival)	2.1
Ictalurus punctatus	9d MATC§	2.4*
Micropterus salmoides	11d MATC§	4.1*
Brachydanio rerio	34d MATC§	10.0
Carassius	7d MATC§	15.6*

auratus		
Pimephales promelas	30d MATC§	18.3*
Invertebrates		
Daphnia magna	NOEC	6.0
Opercularia bimarginata	72h NOEC	10.0
Ceriodaphnia dubia	14d MATC§	13.4
Entosiphon sulcatum	72h NOEC	15.0
Chironomus decorus	96h NOEC	20.0
Paramecium caudatum	72h NOEC	20.0
Amphibians		
Rana pipiens	7d MATC§	20.4*
Bufo fowleri	7d MATC§	48.6*
Bufo americanus	15-23d LOEC	50.0
Ambystoma jeffersonianum	17-25d MATC§	70.7*
Ambystoma maculatum	38-44d MATC§	70.7*
Rana sylvatica	13-23d MATC§	70.7*
Plants		
Elodea canadensis	NOEC	1.0
Spirodella polyrrhiza	10d MATC§	1.8*
Chlorella pyrenoidosa	NOEC	2.0*
Phragmites australis	4 month NOEC	4.0
Chlorella vulgaris	NOEC	5.2
Selenastrum capricornutum	72h LOEC	12.3
Scenedesmus subpicatus	96h EC_{10}	30.0
Myriophyllum spicatum	NOEC	34.2
Anacystis nidulans	NOEC	50.0
Lemna minor	7d NOEC	60.0

*Value shown is the geometric mean of comparable values

§MATC values calculated as the geometric mean of the reported NOEC/L and LOEC/L

Summary statistics for the long-term SSD are presented in Table 5. The 5th percentile on the long-term SSD is 1.5 mg L^{-1} with approximate 95% confidence limits on this mean of 1.2 and 1.7 mg L^{-1}. The CWQG is defined as the 5th percentile on the SSD.

Table 5. Long-term CWQG for Boron Resulting from the SSD Method.

	Concentration
SSD 5th percentile	1.5 mg L^{-1}
Lower 95% confidence limit	1.2 mg L^{-1}
Upper 95% confidence limit	1.7 mg L^{-1}

Therefore, the long-term exposure CWQG for the protection of freshwater life is 1.5 mg L^{-1}, for boron.

Marine Water Quality Guideline: Marine toxicity data was not evaluated to see if there was sufficient data available to derive a short-term or long-term marine water quality guideline for boron.

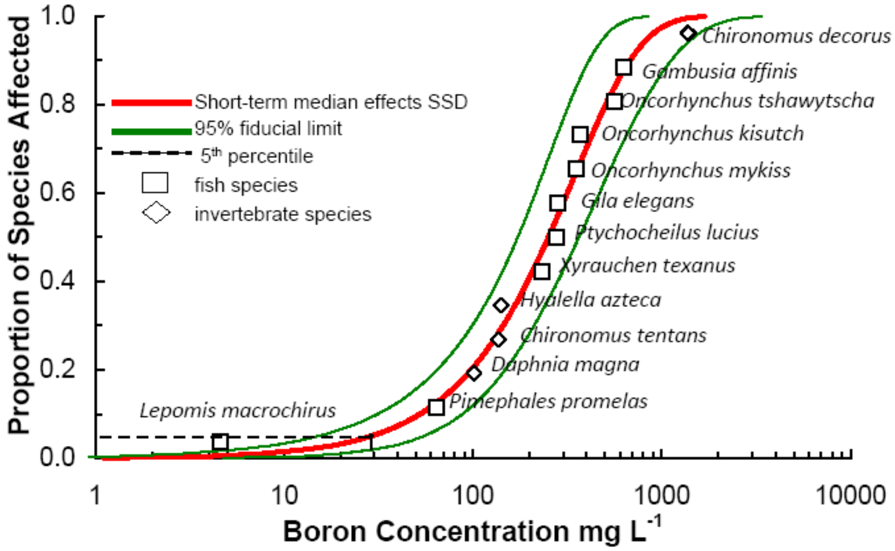

Figure 1. Short-term SSD (log-Gompertz) representing the toxicity of boron in fresh water consisting of acceptable short-term LC50s of thirteen aquatic species versus proportion of species affected.

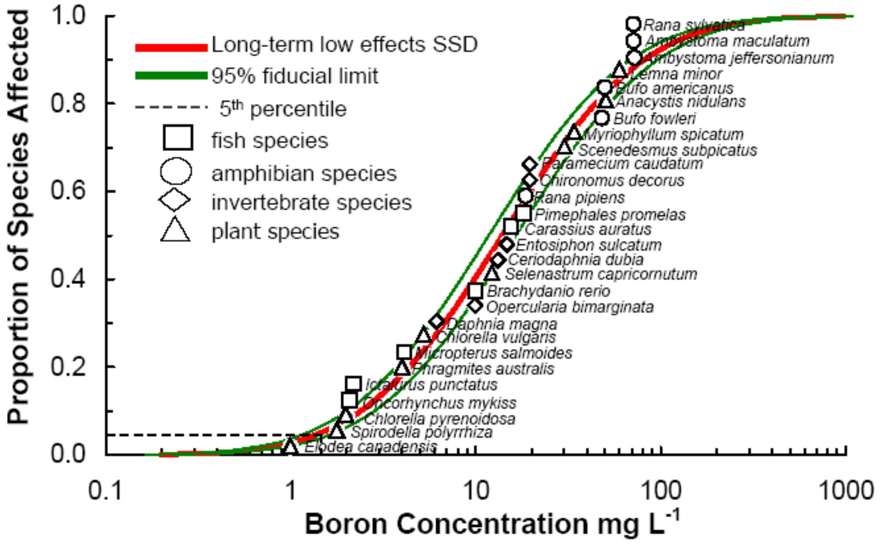

Figure 2. Long-term SSD (log-Normal) representing the toxicity of boron in fresh water consisting of acceptable long-term no- and low-effect endpoints of twenty eight aquatic species versus proportion of species affected.

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For further scientific information, contact:

Ontario Ministry of Environment
Standards Development Branch
40 St. Clair Ave., West
Toronto, ON. M4V 1M2
Phone: (416) 327-5519
E-mail: Tim.Fletcher@ontario.ca
Internet: http://www.ene.gov.on.ca

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